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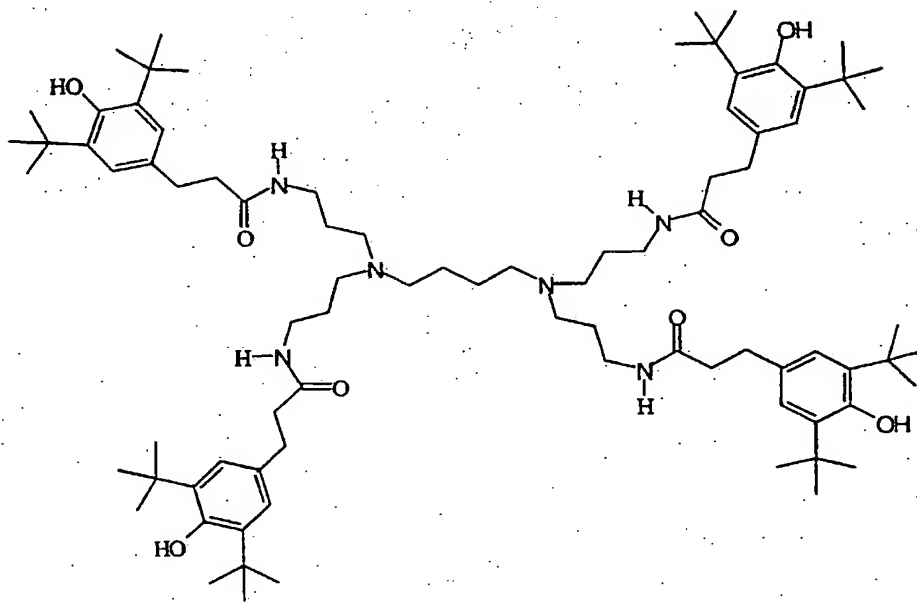
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(54) Title: MULTIFUNCTIONAL THERMO-OXIDATIVE STABILISER



(57) Abstract: The invention relates to a compound with stabilising properties that contains at least one group having an anti-oxidizing effect, at least one -CO-NH-bond and also at least one tertiary amine group. The compound according to the invention exhibits improved performance as a stabiliser in a polymer matrix, for example as thermo-oxidative stabiliser in segmented polyether ester copolymers, as well as a strongly reduced tendency to blooming, so that higher proportions may be used. The invention also relates to a process for the preparation of the compound as well as to application of the mentioned compound as a thermo-oxidative stabiliser. Furthermore the invention also relates to a plastic composition containing the compound with stabilising properties as well as a product obtained with such a plastic composition.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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MULTIFUNCTIONAL THERMO-OXIDATIVE STABILISER

5 The invention relates to a compound with stabilising properties that contains at least one group having an anti-oxidizing effect and at least one -CO-NH- bond. The invention also relates to a process for the preparation of said compound, as well as to application of said compound as a thermo-oxidative stabiliser in a polymer matrix. Furthermore the invention also relates to a plastic composition
10 comprising a polymer matrix and a compound with stabilising properties, as well as to a product obtained with such a plastic composition.

 Within the framework of the present invention a group having an anti-oxidizing effect is understood to be one of the active groups from known anti-oxidants as described for example in Encyclopaedia of Polymer Science and
15 Technology, Volume 15, page 539 et seq., Wiley, New York (1989), ISBN 0-471-80947-0. In the framework of the present invention a -CO-NH- bond is understood to be a bond in which this sequence occurs. Examples are an amide, a urethane or a urea bond.

 Such a compound with stabilising properties is known for example
20 from Chapter 17 of Handbook of Thermoplastics; O. Olabishi (Ed.), Marcel Dekker Inc, New York (1997), ISBN 0-8247-9797-3. In this publication the amide group containing phenolic antioxidant 1,6-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionamide]hexane, which is commercially available as Irganox®
1098 (Ciba), is reported to be one of the most effective thermo-oxidative stabilisers
25 for segmented polyetherester copolymers.

 A disadvantage of the aforementioned compound according to the prior art as a stabiliser for amongst others segmented polyetherester copolymers is that it shows a strong tendency to bloom from the copolymer, so that higher concentrations are not desirable and furthermore, due to the blooming, show a
30 relatively small added stabilising effect. As a consequence of this it is often not possible to meet the ever increasing requirements relating to thermal stability and resistance that are specified for the aforementioned polyetherester copolymers, in particular for applications in the automotive sector.

The object of the invention is to provide a compound with stabilising properties that contains at least one group having an anti-oxidizing effect and at least one -CO-NH- bond, which compound does not exhibit or exhibits to a lesser extent the aforementioned adverse blooming effects and with which enhanced thermo-oxidative stabilisation can be achieved.

The inventors have succeeded in achieving this object with a compound with stabilising properties in which the at least one group having an anti-oxidizing effect comprises a sterically hindered phenol group and/or an aromatic amine group, and which also contains at least one tertiary amine group.

The combination of at least three different functional groups, namely groups with an anti-oxidizing effect, comprising a sterically-hindered phenol and/or an aromatic amine group, -CO-NH- bonds and tertiary amine groups in a single compound yields improved performance as a stabiliser, particularly as a thermo-oxidative stabiliser, in a polymer matrix, as well as a strongly diminished blooming, so that higher proportions may be applied and a higher level of stabilisation can be achieved.

It has been found that the compound according to the invention is especially suited for application as a thermo-oxidative stabiliser for plastics, for example for polycondensates like polyamides or polyesters, for polyethers, or for polyether segments-containing segmented copolymers. The compound is thermally stable, so that mixing with a polymer melt or addition during the polymerisation process is possible.

A further advantage of the compound according to the invention is that through the choice of the quantity and nature of the various functional groups or various building blocks of the compound, the polarity and molecular mass, and so the solubility in or compatibility with the polymer matrix in which the compound is applied as a stabiliser, can be changed as desired. In this respect an additional advantage of the tertiary amine group is, that it can be modified easily to improve the solubility of the compound particularly in polar media, e.g. via quaternisation.

Another advantage is that the stabiliser is already effective in relatively small quantities. Another advantage is that the saturation effect in the stabilising behaviour occurs in a relatively late stage, which means that the stability may be enhanced by increasing the concentration across a wide range. Yet another advantage is that good stabilizing performance is obtained also at relatively high temperatures.

The publication FR-A-2761691 discloses a compound with stabilising properties, which is based on a hyperbranched polymer or a dendrimer and has terminal thiol groups as the at least one group having an anti-oxidizing effect, and which can also contain at least one -CO-NH- bond, and at least one tertiary amine group. Use of this compound as an anti-oxidant is also described, but only in compositions for cosmetic or pharmaceutical application and not in a polymer matrix.

As a group having an anti-oxidizing effect, comprising a sterically hindered phenol or an aromatic amine group, any such group known from thermo-oxidative stabilisers that are described in for example Encyclopaedia of Polymer Science and Technology, Volume 15, page 539 et seq., Wiley, New York (1989), ISBN 0-471-80947-0, can be used.

The compound according to the invention may contain only hindered phenols, only aromatic amines, or both groups. Preferably the compound contains a combination of these groups.

The -CO-NH- bond in the compound according to the invention is for example an amide bond, urethane bond or urea bond. Such -CO-NH- bonds have for example been formed through the reaction of a reactive group X with another reactive group Y, where the reactive groups X and Y are chosen for example from a carboxylic acid group, a carboxylic acid chloride group, a carboxylic anhydride group, an isocyanate group, a hydroxyl group or a primary or secondary aliphatic amine group.

In a special embodiment the compound contains one or more tertiary amine groups that have been converted at least partially into a quaternary ammonium compound, for example by reaction with an alkyl iodide. The structure of the alkyl iodide is an added variable to control the properties, for example polarity, of the compound according to the invention. Thus the compound will obtain a more polar character when the alkyl iodide comprises a short chain, for example methyl iodide. The anion in the quaternary ammonium compound may be varied also, for example through substitution of the iodide ion via an ion exchange process.

Preferably the compound according to the invention contains, besides one or more tertiary amine groups, at least two -CO-NH- bonds and at least two groups with an anti-oxidizing effect. More preferably the compound according to the invention contains one or more tertiary amine groups, at least three -CO-NH- bonds and at least three groups with an anti-oxidizing effect. Still more preferably the compound according to the invention contains at least two tertiary amine groups, at

least four -CO-NH- bonds and at least four groups having an anti-oxidizing effect. The advantage of an increasing number of functional groups is increased stabilising performance and especially a further reduction of the blooming effect.

The molar mass of the compound according to the invention is preferably greater than 300, more preferably greater than 500 and still more preferably greater than approximately 1000 g/mole. An unlimited increase in molar mass may however lead to a reduced instead of improved solubility in a polymer matrix. The molar mass of the compound according to the invention is therefore in general lower than about 10000 g/mole, preferably lower than approximately 6000 g/mole, more preferably lower than approximately 4000 g/mole.

The compound according to the invention is prepared for example by reacting a building block A and a building block B with the formation of at least one -CO-NH- bond, in a manner known to those skilled in the art.

Building block A contains a group having an anti-oxidizing effect, for example a sterically-hindered phenol group or an aromatic amine group, and also a reactive group X, which on reacting with another reactive group results in a -CO-NH- bond. Suitable examples of such a reactive group X are a primary or secondary aliphatic amine group, a hydroxyl group, a carboxylic acid group, a carboxylic acid chloride group, a carboxylic anhydride group or an isocyanate group. Preferably such a reactive group X is linked to the group having an anti-oxidizing effect via an aliphatic or aromatic bonding chain that may contain, besides 2-20 carbon atoms, also a hetero atom, for example N, O, P, S, or Si. Preferably the reactive group X is a carboxylic acid and more preferably an aliphatic carboxylic acid. Very good results have been obtained with the compound 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionic acid. Advantages of the use of this compound are a simple reaction with an amine and the commercial availability (Irganox® 1310, Ciba).

Building block B contains at least one tertiary amine and at least one reactive group Y, preferably chosen from the group of primary or secondary aliphatic amines, hydroxyls, carboxylic acids, carboxylic acid chlorides, carboxylic anhydrides or isocyanates, such that after reaction with the reactive group X a CO-NH- bond results. Preferably building block B contains, besides at least one tertiary amine, at least two reactive groups Y.

Preferably building block B contains, besides at least one tertiary amine, at least two primary or secondary aliphatic amines (polyamine). More preferably building block B contains, besides at least one tertiary amine, at least two

primary amines and still more preferably at least three and most preferably at least four primary amines.

Suitable polyamines that also contain at least one tertiary amine include tertiary amino alkyl amines or branched, strongly branched or star-shaped amino-terminated oligomers or dendrimers, for example polyalkylene amine-based dendrimers described in WO-A9314147, WO-A-952228 and WO-A-9520619. Suitable examples of such polyamines are tris(amino alkyl)amines with an alkyl group having from 1 to 25 carbon atoms, in particular tris(2-aminoethyl)amine, and dendrimers with a nucleus based on a diaminoalkane and with branches, based on acrylonitrile, in particular 4-cascade:1,4 diaminobutane[4]:propylamine ($n = 4$) or 8-cascade:1,4 butanediamine[4]:((1-azabutylydene)⁴:propylamine ($n = 8$) (for the nomenclature of dendrimers refer to G. Newkome et al., J.Poly.,Sci., Part A: Polymer Chemistry, 31 (1993), pages 641-651). Highly suitable is 4-cascade: 1,4-diaminobutane[4]:propylamine ($n = 4$). The advantage of this compound is good thermal stability, the presence of two tertiary and four primary amines and commercial availability.

For that matter, the precursors of the above-mentioned dendrimers, in which nitrile groups are present, are also eminently suitable for preparing building blocks B that contain, besides at least one tertiary amine, at least two carboxylic acid groups or isocyanate groups. For the preparation of such dendrimers the reader is referred to the above-mentioned patent publications.

It is especially preferred to react, as building block B, a polyamine that also contains one or more tertiary amine groups with a building block A that contains, besides a sterically-hindered phenol or an aromatic amine group, also a carboxylic acid group, with the formation of one or more amide bonds. Suitable examples hereof are the reaction of tris(2-aminoethyl) amine with 3-(3,5-di-T-butyl-4-hydroxyphenyl) proprionic acid and the reaction of 4-cascade:1,4-diaminobutane[4]:propylamine ($n = 4$) with 3-(3,5-di-T-butyl-4-hydroxyphenyl)propionic acid, with the molar ratio of amine/carboxylic acid preferably being approximately 1. The structural formula of the latter reaction product, compound 1, is shown in Figure 1.

It is also possible according to the invention to react mixtures of different building blocks A and B, provided that the reactive groups X and Y are selected to react with each other.

The compound according to the invention may contain, besides the

functional groups mentioned, other functional groups, provided that they do not adversely affect the compound's performance as a stabiliser. Such groups may result from incomplete reactions between the reactive groups X and Y of the different building blocks, but may also have been, or may be, introduced intentionally. The
5 advantage of the presence of other functional groups is that the solubility or the compatibility of the compound according to the invention in or with the polymer to be stabilised is optimised.

Examples of such other functional groups are carboxylic acids, carboxylic acid chlorides, carboxylic anhydrides, isocyanates, hydroxyls, thiols,
10 primary or secondary aliphatic amines, quaternary ammonium compounds or combinations thereof.

The compound according to the invention is very suitable for use as a thermo-oxidative stabiliser in a polymer matrix.

The invention also relates to a plastic composition comprising a
15 polymer matrix and a compound with stabilising properties that contains at least one group having an anti-oxidizing effect, at least one -CO-NH- bond, and also at least one tertiary amine group.

The invention also concerns a plastic composition comprising a polymer matrix and a compound with stabilising properties according to the invention.
20 The advantage of such compositions is improved thermo-oxidative stability at relatively high temperatures, without blooming effects.

The polymer matrix may comprise various polymers, for example polyolefins; vinyl polymers; polycondensates, for example polyester, polyamide and polycarbonate; and polyethers, for example polyacetal (POM) and polyether
25 segments-containing copolymers. Examples of such segmented copolymers include segmented polyetherurethane copolymers, segmented polyetheramide copolymers and segmented polyetherester copolymers. The compound according to the invention is particularly suitable for application as thermo-oxidative stabiliser for polycondensates and polyethers, for example segmented polyetherester copolymers.

30 Such segmented polyetherester copolymers, their preparation and properties are described in detail in the aforementioned book Handbook of Thermoplastics and in Thermoplastic Elastomers, G. Holden et al. (Eds), 2nd Ed., Hanser Verlag, Munich, Vienna and New York (1996), ISBN 1-56990-205-4. The segmented polyetherester copolymers contain hard segments made up of units
35 derived from at least one alkylene diol and at least one aromatic dicarboxylic acid or

an ester thereof and soft segments derived from at least one polyalkylene oxide.

The segmented copolyether esters are applied in many areas and offer advantages over other thermoplastic elastomers, for one thing because of superior processability as a result of the presence of the rapidly crystallizing hard polyester segments. Adequate stabilisation is essential for applications that call for good thermal resistance, such as in the automotive industry, particularly for applications in or near the engine compartment.

Most surprisingly, it appears that the stabilising performance of the compound according to the invention in polyetherester copolymers of different compositions, for example with different soft segments, is almost equally good, while stabilisers according to the prior art require optimisation for each polymer.

The plastic composition according to the invention may contain, besides a polymer matrix and the compound with stabilizing properties, other additives such as UV-stabilisers, thermo-oxidative stabilisers that are active via a different mechanism, for example an organic phosphorus compound or a thio-compound, colorants, carbon black, processing aids, for example mould release agents, fillers, flame retardants, etc.

The proportion of the compound according to the invention in the plastic composition may vary as required within broad limits, for example from 0.2 to 5 mass % (relative to the polymer matrix), and is largely dictated by the desired stability level. For high stability a proportion of the compound of at least 0.5 mass % relative to the polymer is preferred, very good stability is obtained from a proportion of approximately 1 mass %, still better stability is obtained from approximately 2 mass %.

Preferably the plastic composition contains a polyether-containing segmented block copolymer, more preferably a segmented polyetherester copolymer.

The invention also relates to a product obtained from the plastic composition using customary processes, for example injection moulding, compression moulding, extrusion and blow-moulding.

The plastic composition according to the invention is particularly applied in objects that are subjected to frequent deformation at elevated temperature. Examples include boots for protection of universal joints in cars, boots for protection of spring systems, air ducts, convoluted tubes, seals, gaskets, etc.

The invention is now further explained with reference to the following examples, without being limited thereto.

The segmented polyetherester copolymers were prepared in the manner described in Thermoplastic Elastomers, 2nd ed. page. 195-197, (1996) Carl Hanser Verlag and the references stated therein, in the presence of 0.02 wt% Irganox 1098, and are commercially available as such. The stated quantities of stabiliser were mixed into the stated copolyetherester in the melt phase. Next, test samples were prepared from the plastic compositions by injection moulding. Test bars for ISO 527 tensile tests were stored in an air-circulation oven at a temperature of 150°C and the tensile strength of a number of samples was measured after different intervals. Sample life-time is defined as the time (in hours) lapsing until the tensile strength diminished to half the initial value. The occurrence of a blooming effect was established visually.

Example I

Compound 1 was synthesized by heating 14.07 g (44.5 mmol) 4-cascade:1,4-diaminobutane[4]:propylamine ($n = 4$) (Astramol®, DSM N.V. NL) and 49.49 g (178 mmol) 3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionic acid (Irganox® 1310, Ciba, CH) in *p*-xylene at 170°C for 22 hours. The reaction product was isolated and the yield was 58 g.

The reaction product was analysed by ¹H-, ¹³C-NMR and IR spectroscopy, and this revealed no sign of free amine groups. The thermal stability of the compound was determined by Thermo-Gravimetric Analysis (TGA). After exposure to a 72/18 N₂/O₂ atmosphere at a temperature of 240°C for 60 minutes, a weight loss of 1.2% (static measurement) had occurred. The degradation temperature was determined at 275°C (5% weight loss in a 72/18 N₂/O₂ atmosphere; dynamic measurement at a heating rate of 20°C/min).

Examples II-IV and comparative experiments A-D

In these experiments the effect was determined of various known stabilisers and of various concentrations of compound 1 on the life-time of a segmented polyetherester copolymer based on ethylene oxide-terminated polypropylene oxide and polybutylene terephthalate with Shore D hardness 58, Arnitel® PL580 (DSM N.V., NL).

The results are summarized in Table 1. Here, I1330 stands for Irganox® 1330 and I1098 for Irganox® 1098, two phenolic antioxidants of Ciba (CH), and N445 for Naugard® 445, an aromatic amine antioxidant of Uniroyal Chemical

(UK). These known antioxidants were applied in the maximum concentration in which Arnitel PL580 did not yet exhibit any distinct blooming effect, as previously established by experimentation.

5

Table 1. Stabilisation of Arnitel® PL580

| | Stabiliser | Concentration (mass %) | Life-time (hours) |
|--------------|------------|---------------------------|----------------------|
| Comp. exp. A | -- | 0 | 40 |
| Comp. exp. B | I1330 | 0.5 | 20 |
| Comp. exp. C | I1098 | 0.2 | 40 |
| Comp. exp. D | N445 | 1.0 | 270 |
| Example II | Compound 1 | 0.25 | 130 |
| Example III | Compound 1 | 0.5 | 250 |
| Example IV | Compound 1 | 1.0 | 280 |

10 These results show that the performance of compound 1 is distinctly better than that of the known antioxidants with phenolic groups and at least comparable with that of the known aromatic amine antioxidant. The samples in Examples II-IV did not exhibit any observable blooming, not even at the high concentrations used.

15 Examples V-VIII and comparative experiments E - H

In these experiments the effect was determined of various known stabilisers and of various concentrations of compound 1 on the life-time of a polyetherester block copolymer based on polytetramethylene oxide and polybutylene terephthalate with Shore D hardness 55, Arnitel® EL550 (DSM N.V., NL). These
20 known antioxidants were applied in the maximum concentration in which Arnitel EL580 did not yet exhibit any distinct blooming effect, as previously established by experimentation.

The results are summarized in Table 2.

25

Table 2. Stabilisation of Arnitel® EL550

| | Stabiliser | concentration (mass %) | Life-time (hours) |
|--------------|------------|---------------------------|----------------------|
| Comp. exp. E | -- | 0 | 40 |
| Comp. exp. F | I1330 | 0.25 | 35 |
| Comp. exp. G | I1098 | 0.2 | 120 |
| Comp. exp. H | N445 | 1.0 | 135 |
| Example V | Compound 1 | 0.25 | 90 |
| Example VI | Compound 1 | 0.5 | 230 |
| Example VII | Compound 1 | 1.0 | 260 |
| Example VIII | Compound 1 | 2.0 | 340 |

- 5 These results show that the performance of compound 1 is distinctly better than, or is comparable with, the known antioxidants with phenolic groups at comparable concentrations but may be improved by increasing the concentration, without any observable blooming occurring, even on 2% addition. The performance of compound 1 with this polymer is distinctly better than that of the known aromatic amine antioxidant.

CLAIMS

1. A compound with stabilising properties that contains at least one group having an anti-oxidizing effect and at least one -CO-NH- bond, characterised in that the at least one group having an anti-oxidizing effect comprises a sterically hindered phenol group and/or an aromatic amine group, and the compound also contains at least one tertiary amine group.
2. A compound according to claim 1, wherein the group having an anti-oxidizing effect is connected with the tertiary amine via a chain containing a -CO-NH- bond.
3. A compound according to one of the claims 1-2, which compound also contains a quaternary ammonium group.
4. A compound according to one of the claims 1-3, which compound also contains at least one other functional group chosen from the group of carboxylic acids, carboxylic acid chlorides, carboxylic anhydrides, isocyanates, hydroxyls, thiols, or primary or secondary aliphatic amines.
5. A compound according to one of the claims 1-4, which compound contains at least three groups having an anti-oxidizing effect and at least three -CO-NH- bonds.
6. A compound according to claim 5, which compound is the reaction product of tris(2-amino ethyl) amine and 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionic acid.
7. A compound according to one of the claims 1-4, which compound contains at least four groups having an anti-oxidizing effect, at least four -CO-NH- bonds and at least two tertiary amine groups.
8. A compound according to claim 7, which compound is the reaction product of 4-cascade:1,4-diaminobutane [4]:propylamine (n = 4) and 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionic acid.
9. A compound according to one of the claims 1-8, which compound has a molar mass of less than approximately 6,000 g/mole.
10. A compound according to one of the claims 1-9, which compound has a molar mass of approximately 500-4,000 g/mole.
11. A process for the preparation of a compound with stabilising properties according to one of the claims 1-10, characterised in that a building block A that contains a group having an anti-oxidizing effect and a reactive group X,

- reacts with a building block B that contains at least one tertiary amine group and at least one reactive group Y, wherein the reactive groups X and Y are chosen from the group of carboxylic acids, carboxylic acid chlorides, carboxylic acid anhydrides, isocyanates, hydroxyls, and primary or secondary aliphatic amines, with the formation of at least one -CO-NH-bond.
- 5
12. A process according to claim 11, wherein the reactive group X is a carboxylic acid and the reactive group Y is an aliphatic amine.
13. A process according to one of the claims 11-12, wherein building block A is 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionic acid and building block B is tris(2-amino ethyl)amine.
- 10
14. A process according to one of the claims 11-12, wherein building block A is 3-(3,5-di-T-butyl-4-hydroxyphenyl)propionic acid and building block B is 4-cascade:1,4-diaminobutane[4]:propylamine ($n = 4$).
- 15
15. Use of the compound with stabilising properties according to one of the claims 1-10 or obtained with the process according to one of the claims 11-14 as thermo-oxidative stabiliser in a polymer matrix.
16. A plastic composition comprising a polymer matrix and a compound with stabilising properties that contains at least one group having an anti-oxidizing effect and at least one -CO-NH- bond, characterised in that the compound also contains at least one tertiary amine group.
- 20
17. A plastic composition comprising a polymer matrix and a compound with stabilising properties according to one of the claims 1-10 or obtained with a process according to one of the claims 11-14.
- 25
18. A plastic composition according to claim 16 or 17, wherein the proportion of the compound is between 0.2 and 5 mass %, preferably between 0.5 and 2.5 mass %, relative to the polymer matrix.
19. A plastic composition according to one of the claims 16-18, wherein the polymer matrix comprises a polycondensate.
- 30
20. A plastic composition according to one of the claims 16-18, wherein the polymer matrix comprises a polyether.
21. A plastic composition according to one of the claims 16-18, wherein the polymer matrix comprises a segmented copolymer with polyether segments.
22. A plastic composition according to one of the claims 16-18, wherein the polymer matrix comprises a segmented polyetherester copolymer.
- 35

23. A product obtained with a plastic composition according to one of the claims 16-22.
 24. A product chosen from the group of hydraulic hoses, convoluted tubes, boots, air-duct systems, seals and gaskets obtained with the plastic composition according to one of the claims 16-22.
- 5

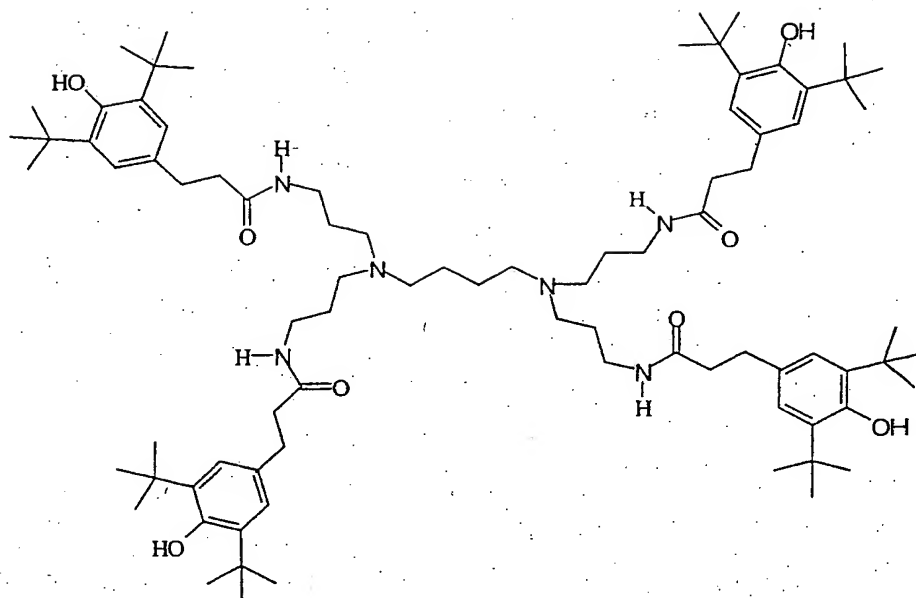


Figure 1.. Structural formula of compound 1

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | US 4 938 885 A (MIGDAL CYRIL A) 3 July 1990 (1990-07-03) claims 1,12 | 1 |
| A | FR 2 761 691 A (OREAL) 9 October 1998 (1998-10-09) claims 1,13,20 page 8, line 20 - line 37 page 9, line 25 - line 39 | 1 |
| A | US 5 714 166 A (BROTHERS II HERBERT M ET AL) 3 February 1998 (1998-02-03) column 37, line 41 - column 38, line 39 | 1 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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